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The application of noble gases and carbon stable isotopes in tracing the fate, migration and storage of CO_2

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Abstract

The noble gases (He, Ne, Ar, Kr and Xe) are present in trace quantities in all natural and engineered CO_2. They have proved to be extremely powerful tracers of both the CO_2 source, and when combined with carbon stable isotopes, the subsurface processes that control the fate of CO_2. Here we present a summary of the progress made over the past decade in using noble gases and stable carbon isotope tracing techniques in CO_2 storage studies. We outline the initial lessons which were learnt from the study of natural CO_2 reservoirs, then show the recent progress that has been made in tracing CO_2 injected into a CO_2-EOR field. We show the application of noble gases in determining natural CO_2 leakage to the shallow groundwater and their use in successfully refuting the allegations of CO_2 leakage made at the Weyburn CO_2-EOR project. Our results illustrate that good progress has been made in using noble gases to determine both the short-term and long-term fate of CO_2 in the subsurface and in the determination of the extent of groundwater interaction that the injected CO_2 has undergone. However, there are still outstanding questions, particularly regarding the exact behaviour of the noble gases compared to CO_2 and we show preliminary results from a laboratory study to investigate how noble gas transport through real rock compares to that of CO_2.

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1. Introduction

The noble gases (He, Ne, Ar, Kr and Xe) are present in trace quantities in all natural and engineered CO_2. There are three distinct sources of noble gases in subsurface fluids (crust, mantle and atmosphere) which are isotopically distinct. Further, they are inert and are not affected by chemical reactions in the reservoir. Consequently the noble gases are extremely powerful tracers of both the CO_2 source and of the subsurface processes that act on CO_2. They have been widely used to trace regional groundwater flow [1, 2] and several studies have successfully demonstrated the potential of noble gases to trace the origins of CO_2 and its fate within reservoirs [3-6].

2. Determining the mechanisms of CO_2 storage in natural CO_2 reservoirs

Noble gas measurements in CO_2 have been used previously to determine that the CO_2 contained within five natural CO_2 reservoirs from the Colorado and Rocky Mountain provinces contained mantle derived CO_2 [6]. This conclusion was based on the high concentration of mantle derived ^3He within the CO_2 reservoirs which resulted in $CO_2/^3He$ ratios within the magmatic range of $1 \times 10^9 - 1 \times 10^{10}$ [7]. Recent work has shown that nine natural CO_2 reservoirs from around the globe show a clear, and quite amazing, correlation between decreasing $CO_2/^3He$ and increasing formation water derived noble gases ^{20}Ne, and crustal derived but groundwater transported ^4He (Fig. 1) [3]. As the noble gases are conservative, the change in $CO_2/^3He$ is due to CO_2 loss and this is quantitatively related to the volume of formation water 'seen' by the gas.

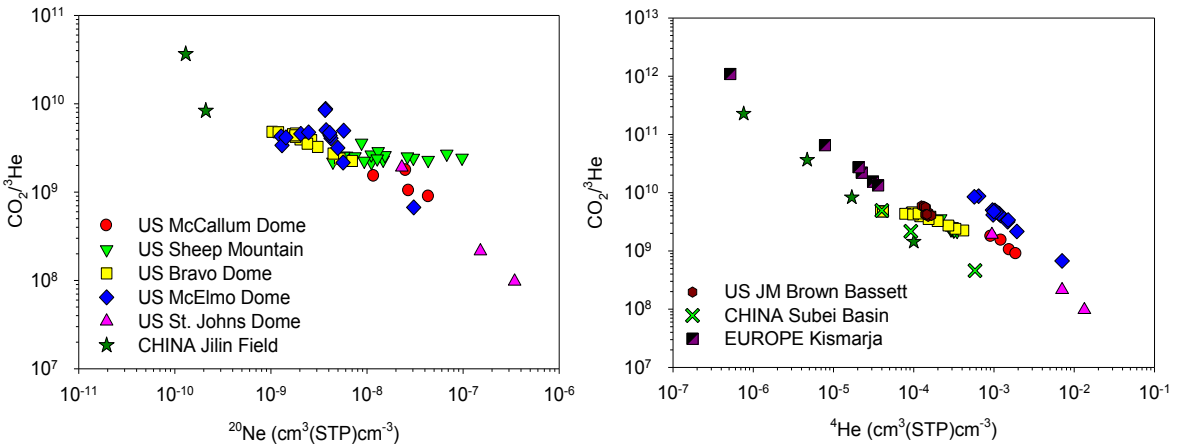


Fig. 1a. Left - $CO_2/^3He$ variation plotted against ^{20}Ne in samples from the 'global' data set of CO_2-rich natural gas fields. There is a general trend in this data set of decreasing $CO_2/^3He$ with increasing ^{20}Ne. ^3He is conservative within the gas phase. Variations in $CO_2/^3He$ therefore represent subsurface changes in CO_2 concentration in the emplaced CO_2 phase. Since the only subsurface source of the ^{20}Ne now in the CO_2 phase is the formation water, the CO_2 sink must be linked to the formation water contacted by the gas phase.

Fig. 1b. Right - The 'global' data sets of CO_2 gas fields also show a strong correlation between decreasing $CO_2/^3He$ and increasing ^4He concentration. ^4He accumulates in formation water over time and underscores the importance of formation water in controlling the mechanism of subsurface CO_2 removal.

Using a combination of the noble gases and carbon stable isotopes it is also possible to differentiate between the amount of CO_2 stored as carbonate mineral precipitate and the amount dissolved in the reservoir formation water. This is because there is a distinct difference between the stable carbon isotopic fractionation which occurs when CO_2 gas dissolves into water and that which occurs when carbonate precipitate is formed [8]. Out of the nine reservoirs studied, only two of them required carbonate precipitation to have occurred to account for the dataset [3].

The Bravo Dome reservoir required the greatest portion of CO_2 precipitation. The carbon stable isotope values exhibit evidence for the maximum amount of carbonate precipitation to be 18% of the total CO_2 volume lost relative to ^3He (Fig. 2a). This is minor in comparison to the 40% of CO_2 that was also dissolved to the formation water within the field (Fig. 2a). The datasets from the other seven fields can all be explained by dissolution of CO_2 into the formation water within a pH range of 5-6. The dissolution trend exhibited by these fields also allows determination of the reservoir pH conditions under which CO_2 dissolution is occurring. This is due to the different carbon stable isotope fractionation factors that result from CO_2(g) dissolving either to HCO_3^- and H_2CO_3 [8].

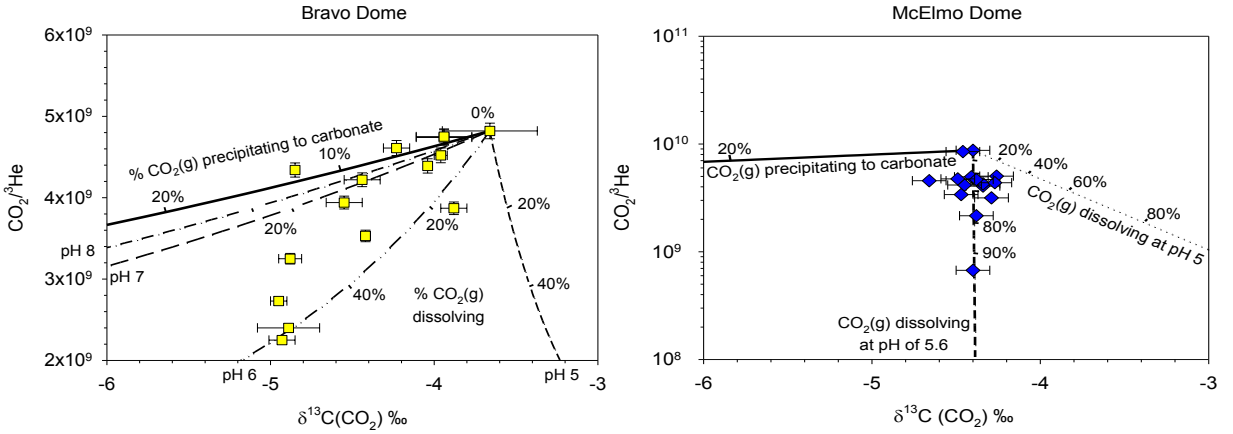


Fig. 2a. Left - $\delta^{13}C(CO_2)$ against $CO_2/^3He$ for Bravo Dome. The solid line shows the predicted trend for carbonate mineral precipitation and the dashed lines show dissolution trends for varying formation water pH. Bravo Dome data is not consistent with the major CO_2 sink being precipitation of carbonate.

Fig. 2b. Right - $\delta^{13}C(CO_2)$ against $CO_2/^3He$ for McElmo Dome. Invariant $\delta^{13}C(CO_2)$ with over an order of magnitude change in $CO_2/^3He$ cannot be accounted for by precipitation (solid line). Dissolution of reservoir CO_2 into formation water at pH=5.6 would produce the observed results.

3. Tracing the migration and fate of CO_2 in the Cranfield EOR reservoir, Mississippi

3.1. Cranfield CO_2-EOR field background and sampling history

The Cranfield CO_2-EOR field is located in southwest Mississippi, ~20 km east of Natchez. The reservoir was discovered in 1943 and oil and gas production first commenced in 1944. The field consists of a simple dome structure, with a gas cap and associated down-dip oil ring. Pressure maintenance was achieved by gas recycling until the gas cap was depleted in 1959. It was subsequently abandoned in 1966 after unsuccessful water injection tests in 1958-59. The field was re-entered for CO_2 injection for EOR in July 2008 by Denbury Resources Inc. Prior to injection the reservoir re-equilibrated to hydrostatic pressure by groundwater infiltration after abandonment. Continuous CO_2 injection without water injection means that Cranfield can be considered as an analogue for injection into a saline aquifer. This is significant as saline formations offer the vast majority of available global CO_2 storage capacity [9-11].

The CO_2 injected into the Cranfield oil field for EOR is sourced from the Jackson Dome natural CO_2 reservoir, located to the northeast of Jackson, MS. The CO_2 contained in Jackson Dome is sourced from the mantle [12] and has a mantle rich noble gas fingerprint. The Jackson Dome CO_2 is piped to Cranfield via a 400km long high pressure CO_2 pipeline. At Cranfield CO_2 and methane is separated from the produced gas and oil, and mixed with incoming Jackson Dome CO_2 and re-injected [13]. The amount of produced gas being recycled into the field has increased significantly with time. Between July 2009 and January 2013 the proportion of recycled gas increased from ~9 to ~30 % of the total injected gas [10]. In April 2010 the CO_2 injection rate reached one million metric tonnes per annum, and by January 2013 6.8 million metric tonnes of CO_2 had been injected, of which 4 million had

been retained in the reservoir [10, 14].

Sampling of the produced and injected gases from the Cranfield CO_2-EOR field was undertaken in 2009 and 2012. In 2009, 9 production wells and an injection well (containing a mixture of Jackson Dome CO_2 and gas recycled from the oil field) were sampled. In 2012, the 9 production wells sampled in 2009 were resampled along with an additional 3 wells which had been drilled between 2009 and 2012, and the same injection well which had been sampled in 2009. Additionally a sample of Jackson Dome CO_2 was taken from the pipeline supplying CO_2 to the Cranfield oil field prior to any mixing of this CO_2 with recycled gas from the field. All samples were collected at high-pressure wellheads. The CO_2 supply pipeline and injection wells were maintained at ~207 bar and ~32°C to keep CO_2 as a supercritical phase. The production wells produce oil, water and gas (comprised predominantly of CO_2 and CH_4) therefore samples were taken from the top of the flow line to avoid sampling liquid. Production wells were operating at pressures between ~8 and ~91 bar and ~62°C.

3.2. Results

The CO_2 piped from Jackson Dome to the Cranfield CO_2-EOR field is comprised almost entirely of CO_2 (99%) with a trace amount of CH_4 and noble gases making up the remainder. $\delta^{13}C_{CO2}$ of this CO_2 is -2.9 ‰, the $^3He/^4He$ is 5.4 R_A (Fig. 3a) and $^{40}Ar/^{36}Ar$ is 4,268. These data are consistent with previous measurements made from samples collected at the Jackson Dome natural CO_2 field [12]. The injected gas sampled in 2009 and 2012 is significantly different from the Jackson Dome CO_2 composition piped to the field. The CO_2 content is lower; 96% (2009) and 87% (2012). $^3He/^4He$ and $^{40}Ar/^{36}Ar$ have also decreased over time (from 4.73 to 4.00 R_A, and 2,909 to 2,723 respectively). These temporal changes are qualitatively consistent with the increased proportion of (methane-free) recycled production gas in the injected gas; ~9% in 2009 and ~30% in 2012 [10]. The $\delta^{13}C$ of the CO_2 injected in 2009 is -2.5 ‰ and -3.6 ‰ in 2012. There is no systematic change compared to Jackson Dome (-2.9 ‰), probably reflecting the variability in the isotopic composition of the recycled produced gas.

The produced gases show an increase in the proportion of injected gas with time. This is shown by a consistent increase in the concentration of CO_2 in the nine wells which were sampled in 2009 and 2012. The noble gas fingerprints in the produced gases become consistently closer to that of the injected gas over time, with increases in $^3He/^4He$, $^{40}Ar/^{36}Ar$ and $^{20}Ne/^{36}Ar$ ratios and a decrease in ^4He, ^{20}Ne and ^{40}Ar concentrations (Fig. 3a). However, in our preliminary data there is no systematic change in the range of $\delta^{13}C_{CO2}$ at these wells. In all cases $^4He/^{20}Ne$ are at least five orders of magnitude higher than the atmospheric value of 0.32 [15] immediately ruling out any contamination from atmosphere during sampling or analysis.

3.3. Tracing the fate of injected CO_2

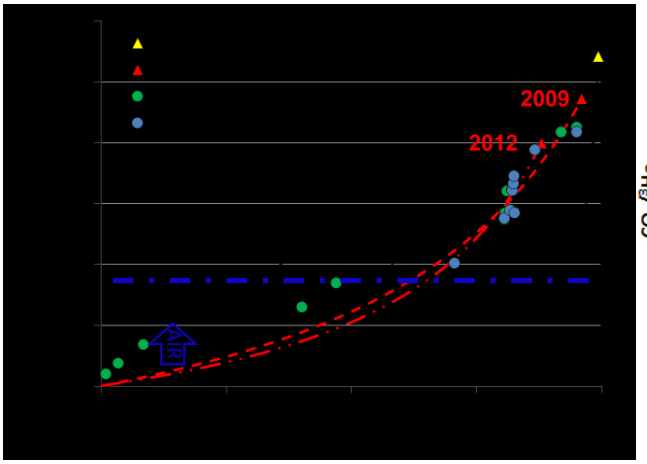
3.3.1. Evidence for two component mixing - $^3He/^4He$ and CO_2 concentrations

The helium isotope data show clear two-component mixing. The majority of the data plot on modelled mixing curves (solid lines) between the mantle dominated injected gas and an in-situ crustal dominated natural gas end-member (using a $^3He/^4He$ of average crust of 0.02 R_A [16] and ^4He concentration of 165 ppm based on the average of the four samples with the lowest $^3He/^4He$ and CO_2 concentrations). However, five of the samples from 2009 do not plot on the mixing line between the in-situ crustal end member and the 2009 injected gas. All of these samples have CO_2 concentrations which are below 50%. These samples could be explained by either addition of an atmospheric air component with a $^3He/^4He$ ratio of 1 or loss of CO_2 relative to He. As the $^4He/^{20}Ne$ ratios are consistently five orders of magnitude higher than the atmospheric value, the addition of an atmospheric air component can be ruled out. Hence, these samples must have lost CO_2 relative to the noble gases.

3.3.2. Evidence for CO_2 loss - $CO_2/^3He$ and CO_2 concentration

As outlined in Section 2 and in several previous studies, $CO_2/^3He$ ratios have provided a useful means of

identifying the fate of CO_2 in natural CO_2 reservoirs. Hence, we investigated the relationship between $CO_2/^3He$ ratios and CO_2 concentration in the Cranfield produced gas samples. Figure 3b clearly shows that four of the five samples with low CO_2 concentrations also have correspondingly lower $CO_2/^3He$ ratios of between 4.02 x 10^8 to 1.24 x 10^9, compared to the range of 3.15 x 10^9 to 4.15 x 10^9 exhibited by the remainder of the samples. The range of higher values is similar to that of the injected CO_2 of 2.77 x 10^9. This clearly implies that the four samples which plot above the two component mixing lines in Fig 3a must have lost a proportion of the CO_2 component relative to ^3He.



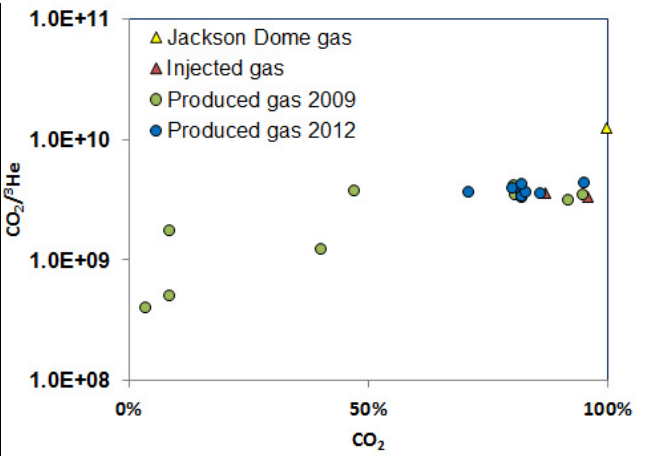


Fig. 3a. Left – $^3He/^4He$ against CO_2 for all Cranfield CO_2-EOR field samples. The dashed black line shows the two component mixing line for the piped Jackson Dome CO_2 mixing with a crustal end member with a $^3He/^4He$ ratio of 0.02 R_A. The two dashed red lines show the calculated 2 component mixing line for the gas injected into the Cranfield CO_2-EOR field in 2009 and 2012 mixing with the same crustal end member. The dashed blue line shows the atmospheric air 3He/4He ratio of 1Ra. It ca be clearly seen that five of the 2009 samples do not plot on the mixing lines between the in-situ crustal end member and the two injected gas compositions.

Fig. 3b. Right - $CO_2/^3He$ against CO_2 concentration for all Cranfield CO_2-EOR field samples. It is clear that four of the five samples with low CO_2 concentrations also have correspondingly lower $CO_2/^3He$ ratios, compared to the consistently similar range to the injected gas exhibited by the remainder of the samples.

3.3.3. Evidence for CO_2 dissolution into the formation water - $CO_2/^3He$, ^{20}Ne and ^4He

As described earlier, natural CO_2 reservoirs show a strong correlation between decreasing $CO_2/^3He$ and increasing ^{20}Ne and ^4He concentrations. Since the only subsurface source of ^{20}Ne in the CO_2 phase within natural CO_2 reservoirs is the formation water, the CO_2 sink must be linked to the formation water contacted by the gas phase. ^4He accumulates in formation water over time and underscores the importance of formation water in controlling the mechanism of subsurface CO_2 removal and hence the increases in both ^{20}Ne and ^4He corresponding to $CO_2/^3He$ decrease provides strong evidence of the dissolution of CO_2 into the formation water. Figure 4 shows that there is a clear increase in both ^{20}Ne and ^4He concentrations in the four samples which show lower $CO_2/^3He$ ratios, compared to the majority of the produced gases and the injected gas. This is identical to the relationships observed in natural CO_2 reservoirs, which indicates that in the four samples in question, free phase CO_2 has been lost by dissolved into the formation water.

The majority of samples, however, have $CO_2/^3He$ within the average magmatic value similar as that of the gas injected into the Cranfield CO_2-EOR field. This indicates that minimal dissolution of CO_2 into the formation water has occurred in these samples. This suggests that the majority of injected CO_2 stays as a free phase and is physically/residually trapped. These preliminary results are the first that illustrate how well noble gas fingerprints are preserved in CO_2-EOR field and demonstrates how they help us identify and quantify CO_2 trapping mechanisms and interaction history in the reservoir.

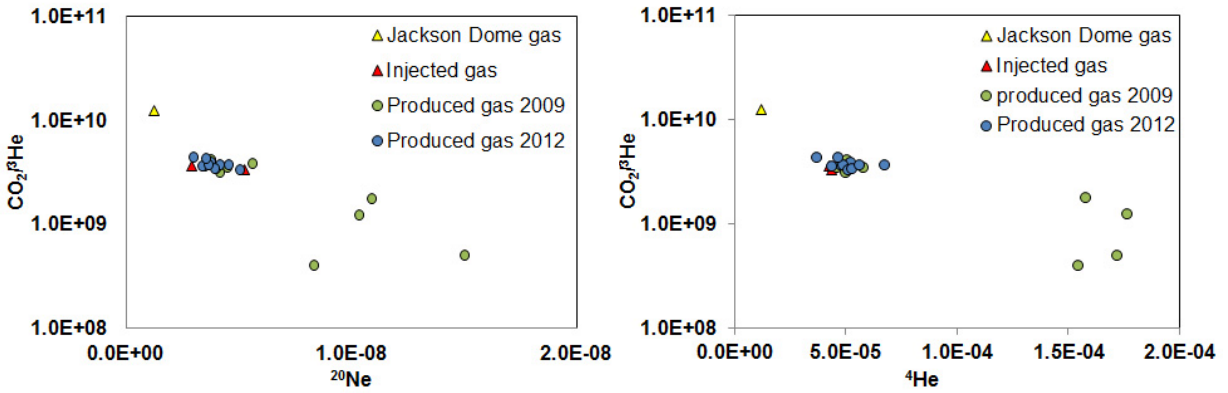


Fig. 4a. Left – $CO_2/^3He$ against ^{20}Ne for all Cranfield CO_2-EOR field samples. There is an order of magnitude more ^{20}Ne in the 4 samples which show lower CO_2/3he ratios, which is strikingly similar to the relationship observed in natural CO_2 reservoirs and strong evidence for the loss of free phase CO_2 relative to 3He as a result of CO_2 dissolution into the formation water.

Fig. 4b. Right - $CO_2/^3He$ against ^4He concentration for all Cranfield CO_2-EOR field samples. Again the four samples with lower $CO_2/^3He$ ratios exhibit higher ^4He concentrations, similar to the relationship observed in natural CO_2 reservoirs and further evidence of the dissolution of CO_2 into the formation water, as being the sink of the free phase CO_2 lost relative to ^3He.

4. Using Noble gases to identify and refute CO_2 leakage

4.1. Identifying natural CO_2 migration above the St. Johns Dome natural CO_2 reservoir

In addition to tracing both the migration and fate of CO_2 in natural CO_2 reservoirs, noble gases have proven to be powerful tracers of the natural migration of CO_2 to the surface above a natural CO_2 reservoir. Extensive travertine deposits surround the St. Johns Dome natural CO_2 reservoir, located on the border of Mid-Arizona/New Mexico, USA, highlighting a past history of migration of CO_2 rich fluids to the surface. Despite this historical evidence, no travertine formation is occurring at present and no gaseous CO_2 seeps are currently found in the area [17]. However, high concentrations of HCO_3^- are common in surface springs, shallow groundwater wells used for irrigation and deeper wells used to obtain cooling water for a coal fired power plant in the region. Previous chemical analysis of these waters implied a possible connection between the formation water within the CO_2 reservoir below and the HCO_3^- rich water in the near surface. This link was not found to be conclusive, due to significant differences in water types [17] and the fact that a soil gas survey surrounding these springs and wells was unable to differentiate additional CO_2 flux from that of background biological activity [18].

The production of radiogenic isotopes - such as ^4He and ^{40}Ar - by decay of U, Th and K in the local rocks presents a clear way of determining both the age of and original source of subsurface gases. Identification of significantly above atmospheric levels of ^4He were obtained from both groundwater wells and surface springs samples which directly overlay the natural CO_2 reservoir, implying the addition of a crustal component that had accumulated radiogenic ^4He. Thus, a portion of the water originated at depth, having circulated in the crust for a significant period of time [19]. The ^4He excess was further illustrated by the significantly above air $^4He/^{20}Ne$ measured in all water samples, bar three springs which had low HCO_3^- values and were located significantly away from the CO_2 reservoir. Figure 5a shows that the majority of the surface spring waters and all of the groundwater well waters have $^3He/^4He$ ratios which are below the air ratio indicating that deep ^4He and deep CO_2 from the CO_2 field is present in the waters.

This clearly illustrated that the excess ^4He fingerprint entrained at depth was retained after migration of the waters to the surface. The simplest explanation is that the groundwater wells sampled shallow well and spring waters containing noble gases together with magmatic CO_2 derived from the deep reservoir. In this model, the high concentrations of HCO_3^- present in the sampled waters are then the direct result of the migration of dissolved CO_2

from the deep reservoir, illustrating for the first time that CO_2 can be fingerprinted from source to surface using noble gases, particularly He. Similar noble gas fingerprinting methods have also been recently used to detect the micro-seepage of CO_2 and CH_4 above the Teapot Dome oil field in Wyoming [20].

4.2. Refuting claims of CO_2 leakage above the Weyburn CO_2-EOR field

In January 2011 it was extensively reported that the Kerr family had been forced to move from their property located above the Weyburn-Midale Monitoring and Storage Project in Saskatchewan, Canada. A geochemical consultant from Petro-Find GeoChem Ltd., who was hired on behalf of the Kerr's, reported measurements of $\delta^{13}C$ (CO_2) isotope values in soil gases rich in CO_2 which were similar to those of the CO_2 injected into the deep oil reservoir [21]. The Petroleum Technology Research Centre (PTRC), who are responsible for the environmental monitoring of the Weyburn CO_2-EOR and storage operation, published a detailed response correctly stating that Petrofind had not taken the similar baseline $\delta^{13}C$ (CO_2) isotope measurements conducted prior to the injection into account [22]. Also as $\delta^{13}C$ (CO_2) is not a unique tracer, there were several other natural sources that could account for the measured values. Whilst this response went some way to addressing the public perception fears raised by the alleged CO_2 leakage claims, it was clear that more research was required to re-establish confidence in the safety and security of CO_2 stored at Weyburn. This was imperative for both the project itself and the future acceptance of the safety and security of CO_2 storage technologies. The International Performance Centre for Geologic Storage of CO_2 (IPAC-CO_2) undertook a detailed independent incident response protocol focused on the near surface soil gases, the noble gas composition of the shallow groundwaters and a hydrogeological analysis. In the following section we summarise the findings of the noble gas investigation.

In order to determine if migration of dissolved CO_2 from the Weyburn oil field was responsible for the alleged CO_2 anomaly, we completed noble gas measurements on water samples collected from four groundwater wells surrounding the Kerr quarter, near Goodwater in Saskatchewan. These were compared to the noble gas composition measured from fluids obtained from a production well and CO_2 and water obtained from two separate injection wells on the Weyburn-Midale oil field, located near to the Kerr quarter. The aim of the work was to test the hypothesis that migration of dissolved CO_2, originating from either the free phase CO_2 or water injected into the Weyburn-Midale oil field or from CO_2 contained in the produced fluids, was responsible for the CO_2 anomaly reported at the surface. This focused on dissolved CO_2 in the groundwaters as no free phase CO_2 was present in the sampled well waters and as recent research has shown that the sensitivity of He as a tracer is two orders of magnitude greater in groundwaters than in soil gases [20].

We observed no relationship between the $^3He/^4He$ ratio and HCO_3^- concentrations measured in the groundwaters from the Kerr site (Figure 5b). This is in stark contrast to the systematic relationship observed between HCO_3^- concentration and $^3He/^4He$ ratios in the St. Johns surface springs and groundwater wells (Section 4.1 and Figure 5b). In the Kerr groundwaters increased HCO_3^-, indicating increasing concentrations of dissolved CO_2 did not result in any variation in the air like $^3He/^4He$ ratios. There was also no relationship observed between $^3He/^4He$ ratios and the concentration of ^4He in the Kerr groundwaters. This strongly implied that there is no addition of deep crustal ^4He to the sampled waters surrounding the Kerr quarter and indicates that there was no migration of fluids from depth into the sampled wells. This was again in contrast to the clear relationship between decreasing $^3He/^4He$ and increasing ^4He concentrations observed in the St. Johns groundwaters.

All of the other noble gas (Ne, Ar, Kr) concentrations and the majority of noble gas ratios measured in the groundwaters from wells surrounding the Kerr quarter were within or very close to the air saturated values. We found no evidence in any of the noble gas data that there was any presence of deep crustal derived noble gases within the groundwaters surrounding the Kerr quarter, and hence no evidence of the migration of deep CO_2 from the Weyburn oil field into the groundwater on the Kerr quarter or the surrounding area.

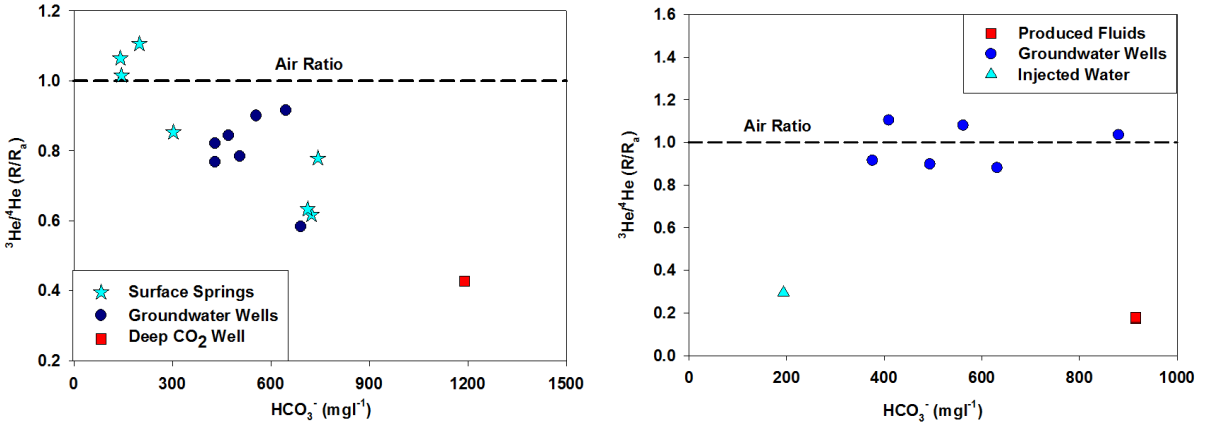


Fig. 5a (left) Plot of $^3He/^4He$ against HCO_3^- for waters sampled near to the natural St. Johns Dome CO_2 field, AZ. Here, the majority of the surface spring waters and all of the groundwater well waters have $^3He/^4He$ ratios which are below the air ratio indicating that deep ^4He and deep CO_2 from the CO_2 field is present.

Fig. 5b (right) Plot of $^3He/^4He$ against HCO_3^- concentration for samples collected at Weyburn. The shallow groundwaters sampled had air $^3He/^4He$, completely different to the CO_2 injected into the storage site or produced water. This shows that there was no CO_2 leakage to the groundwaters.

5. Comparing noble gas and CO_2 flow profiles through real rock

5.1. Introduction

Despite the good progress which has been made in using noble gases as tracers of CO_2 migration and fate there are still outstanding questions, particularly regarding the flow behavior of the noble gases compared to CO_2. Experimental work is underway at the University of Edinburgh to further constrain the factors and processes involved in noble gas and CO_2 transport. We are using unique experimental equipment to determine the factors affecting the transport of noble gases relative to CO_2. This work aims to investigate how noble gases could be used as effective early warning tracers of CO_2 migration in engineered CO_2 storage sites. The experimental system is designed to load a sample loop with a desired gas mixture, which at a given time can be released into a feeder stream as a pulse through the flow cell. The flow cell consists of an air dried 98cm x 3.6cm core of the Fell Sandstone surrounded by aluminium foil and treated with epoxy resin to provide air tight stable conditions. The core is encased upstream and downstream by gas dispersion plates to allow unobstructed gas flow. Real-time analysis of the arrival peaks of the gases downstream is recorded using a HPR20-QIC Quadrupole Mass Spectrometer (QMS).

5.2. Noble Gas and CO_2 Pulse Experiments

He and Ar pulses have been flowed through a CO_2 carrier gas and the arrival profiles measured (Fig 6). The peak arrival times of Ar were similar to that of He; however, and significantly, He arrival was marginally slower at each pressure. The differences in peak arrival times between the He and Ar curves increased as the pressure decreased and the curve profiles for the two noble gases systems differ greatly. The Ar curve profiles also show a steeper angle for initial appearance, but have a longer tail than the He curves do. The CO_2 pulses were passed through a N2 carrier gas. The CO_2 pulses yield slower peak arrival times compared to those of both He and Ar (Fig. 6).

These results are significantly different from the curves predicted by modelling with the arrival times of all gases in the flow experiments being an order of magnitude faster than models predict. Additionally modelling predicts that He should appear the quickest out of the three gas mixtures and it should have had the best retention of the three gases. However, He takes longer to arrive than Ar and exhibits a shorter duration peak. This is because the current

standard modelling techniques do not account for any dispersion taking place. It is clear that that this process is greatly affecting the time it takes the gases to reach the sampling point downstream. He is susceptible to routes that a larger molecule such as CO_2 would be too large to pass through. As a result current model will tend to overestimate the transport rates of the noble gases through the porous media.

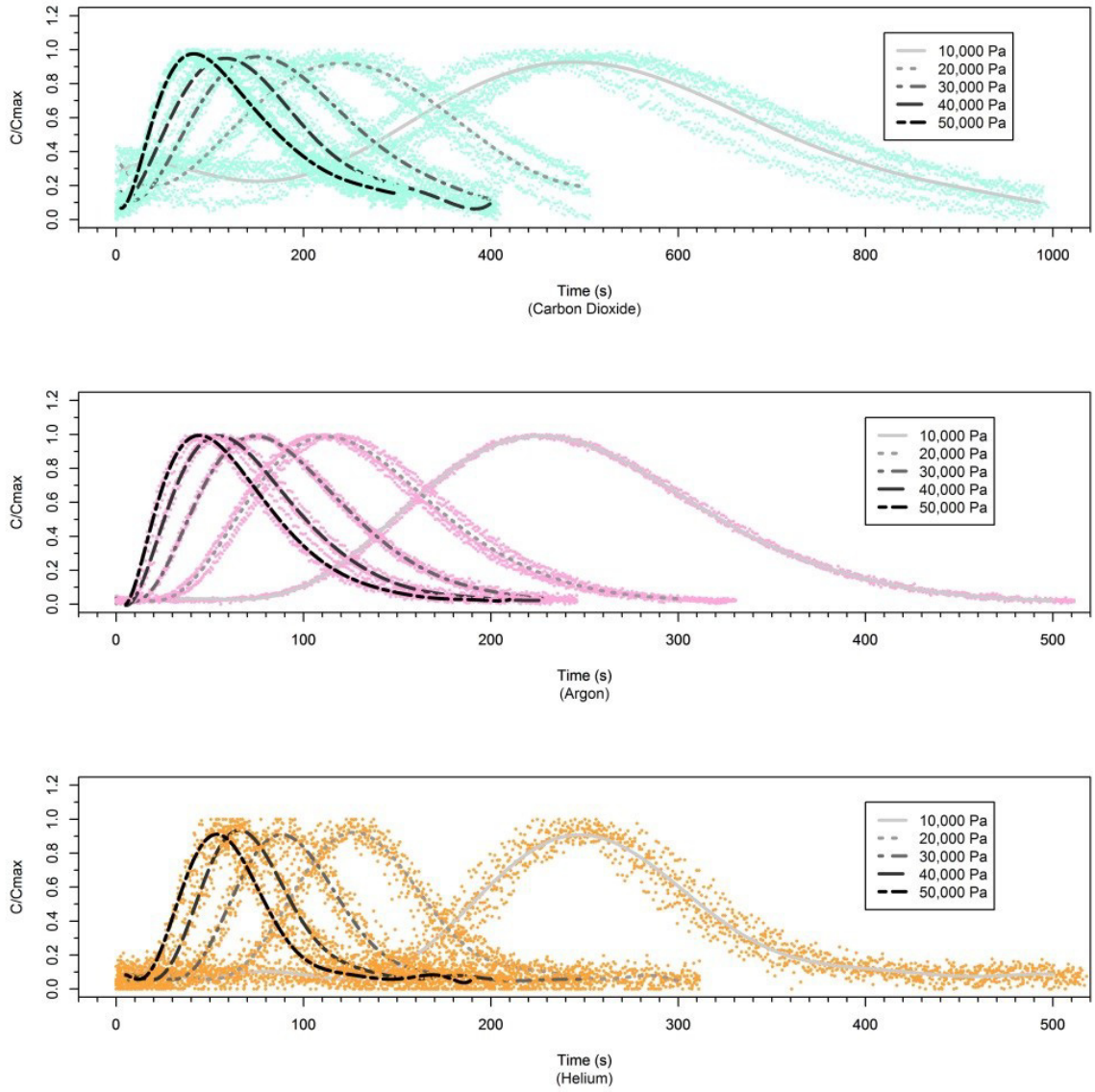


Fig. 6. Experimental results of flow experiments through the flow cell. Experiments were carried out over five different pressures. Each experiment was replicated five times. Results are plotted as scatter plots (cyan for CO_2, pink for argon, orange for helium). Regression lines have been plotted to represent the relationship between the gas concentrations (C/C_{max}) over time (s) as an average of the five experiments.

This preliminary data is the first step in determining how the travel times of CO_2, He and Ar behave relative to each other in porous media. It is our intention to expand this research to the remainder of the noble gases (excluding

Rn). As shown in these early results, the noble gases may be susceptible to enter smaller pore spaces routes that a CO_2 molecule is too large to pass through. Partitioning of the noble gases between the CO_2 and other phases present will also occur – this will need to be considered. Upscaling of these results will determine how effective the different noble gases could be at acting as early warning tracers of CO_2 migration within and out with real world storage sites.

6. Summary and Conclusions

The work documented here illustrates that good progress has been made in using noble gases in tracing the origin, migration and fate of both natural and anthropogenic CO_2. Given the breadth of the applications of noble gases in CO_2 storage and monitoring it is imperative that the progress made in this field is continued. It is therefore essential that future pilot and early industrial scale CO_2 injection studies continue to investigate the behaviour of noble gases in the subsurface in order to help develop suitable noble gas monitoring strategies for universal deployment in the future.

References

[1] M.C. Castro, P. Goblet, E. Ledoux, S. Violette, G. de Marsily, Noble gases as natural tracers of water circulation in the Paris Basin 2. Calibration of a groundwater flow model using noble gas isotope data, Water Resouces Research, 34 (1998) 2467-2483.

[2] M.C. Castro, P. Goblet, Calibration of regional groundwater flow models: Working toward a better understanding of site-specific systems, Water Resouces Research, 39 (2003) 1172.

[3] S.M.V. Gilfillan, B.S. Lollar, G. Holland, D. Blagburn, S. Stevens, M. Schoell, M. Cassidy, Z. Ding, Z. Zhou, G. Lacrampe-Couloume, C.J. Ballentine, Solubility trapping in formation water as dominant CO_2 sink in natural gas fields, Nature, 458 (2009) 614-618.

[4] G.J. Nimz, G.B. Hudson, The use of noble gas isotopes for monitoring leakage of geologically stored CO_2, in: D.C. Thomas, S.M. Benson (Eds.) Carbon Dioxide Capture for Storage in Deep Geologic Formations, Elsevier, 2005, pp. 1113-1128.

[5] S. Lafortune, M. Moreira, P. Agrinier, A. Bonneville, H. Schneider, H. Catalette, Noble gases as tools for subsurface monitoring of CO_2 leakage, Energy Procedia, 1 (2009) 2185-2192.

[6] S.M.V. Gilfillan, C.J. Ballentine, G. Holland, B. Sherwood Lollar, S. Stevens, M. Schoell, M. Cassidy, The noble gas geochemistry of natural CO_2 gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA, Geochimica et Cosmochimica Acta, 72 (2008) 1174-1198.

[7] B. Marty, A. Jambon, C/^{3}He in volatile fluxes from the solid Earth: Implications for carbon geodynamics, Earth and Planetary Science Letters, 83 (1987) 16-26.

[8] P. Deines, D. Langmuir, R.S. Harmon, Stable carbon isotopes and the existence of a gas phase in the evolution of carbonate groundwaters, Geochimica et Cosmochimica Acta, 38 (1974) 1147 - 1184.

[9] J. Lu, Y.K. Kharaka, J.J. Thordsen, J. Horita, A. Karamalidis, C. Griffith, J.A. Hakala, G. Ambats, D.R. Cole, T.J. Phelps, M.A. Manning, P.J. Cook, S.D. Hovorka, CO_2–rock–brine interactions in Lower Tuscaloosa Formation at Cranfield CO_2 sequestration site, Mississippi, U.S.A, Chem. Geol., 291 (2012) 269-277.

[10] S.D. Hovorka, T.A. Meckel, R.H. Treviño, Monitoring a large-volume injection at Cranfield, Mississippi—Project design and recommendations, Int. J. Greenh. Gas Con., 18 (2013) 345-360.

[11] S.D. Hovorka, T.A. Meckel, R.H. Trevino, J. Lu, J.-P. Nicot, J.-W. Choi, D. Freeman, P. Cook, T.M. Daley, J.B. Ajo-Franklin, B.M. Freifeild, C. Doughty, C.R. Carrigan, D.L. Brecque, Y.K. Kharaka, J.J. Thordsen, T.J. Phelps, C. Yang, K.D. Romanak, T. Zhang, R.M. Holt, J.S. Lindler, R.J. Butsch, Monitoring a large volume CO_2 injection: Year two results from SECARB project at Denbury's Cranfield, Mississippi, USA, Energy Procedia, 4 (2011) 3478-3485.

[12] Z. Zhou, C.J. Ballentine, M. Schoell, S.H. Stevens, Identifying and quantifying natural CO_2 sequestration processes over geological timescales: The Jackson Dome CO_2 Deposit, USA, Geochimica et Cosmochimica Acta, 86 (2012) 257-275.

[13] J.-W. Choi, J.-P. Nicot, S.A. Hosseini, S.J. Clift, S.D. Hovorka, CO_2 recycling accounting and EOR operation scheduling to assist in storage capacity assessment at a U.S. gulf coast depleted reservoir, Int. J. Greenh. Gas Con., 18 (2013) 474-484.

[14] S.A. Hosseini, H. Lashgari, J.W. Choi, J.-P. Nicot, J. Lu, S.D. Hovorka, Static and dynamic reservoir modeling for geological CO_2 sequestration at Cranfield, Mississippi, U.S.A, Int. J. Greenh. Gas Con., 18 (2012) 449-462.

[15] M. Ozima, F.A. Podosek, Noble Gas Geochemistry (2nd Ed.), Cambridge University Press, Cambridge, 367., 2001.

[16] J.N. Andrews, The isotopic composition of radiogenic helium and its use to study groundwater movement in confined aquifers, Chemical

Geology, 49 (1985) 339-351.

[17] J. Moore, M. Adams, R. Allis, S. Lutz, S. Rauzi, Mineralogical and geochemical consequences of the long-term presence of CO_2 in natural reservoirs: An example from the Springerville-St. Johns Field, Arizona, and New Mexico, U.S.A, Chemical Geology, 217 (2005) 365.

[18] R. Allis, D. Bergfeld, J. Moore, K. McClure, C. Morgan, T. Chidsey, J.E. Heath, B. McPherson, Implications of results from CO_2 flux surveys over known CO_2 systems for long-term monitoring, in: Fourth Annual Conference on Carbon Capture and Sequestration, DOE/NETL, 2005.

[19] T. Torgersen, W.B. Clarke, Helium accumulation in groundwater, (i): An evaluation of sources and the continental flux of crustal ^4He in the Great Artesian Basin, Australia, Geochimica et Cosmochimica Acta, 49 (1985) 1211-1218.

[20] S.J. Mackintosh, C.J. Ballentine, Using $^3He/^4He$ isotope ratios to identify the source of deep reservoir contributions to shallow fluids and soil gas, Chemical Geology, 304–305 (2012) 142-150.

[21] P. Lafleur, Geochemical Soil Gas Survey - A site investigation of SW30-5-13-W2M, Weyburn Field, Saskatchewan, in: Petro-Find Geochem Ltd., Saskatoon, 2010.

[22] Petroleum Technology Research Centre, Response to a soil gas study by Petro-Find Geochem Ltd., in, 2011.